Metalate Complexes

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From Storable Sources of Atomic Nb^- and Ta^- Ions to Isolable Anionic Tris(1,3-butadiene)metal Complexes: $[M(\eta^4\text{-}C_4H_6)_3]^-$, M = Nb, Ta**

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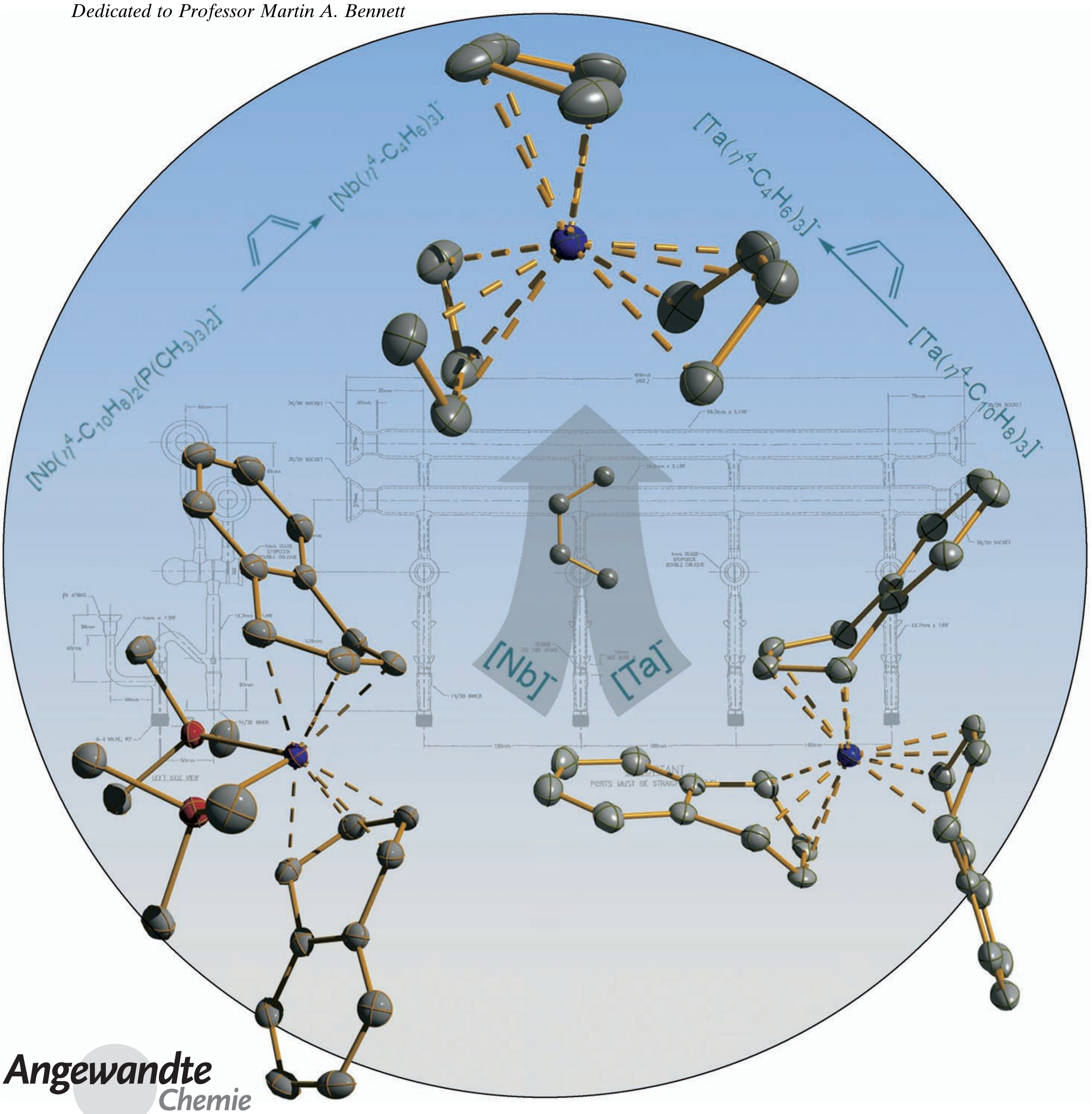
Dedicated to Professor Martin A. Bennett



Kündig and Timms[1] as well as Elschenbroich and Möckel[2] independently prepared and isolated the first homoleptic naphthalene complexes of zero-valent metals ($[\mathrm{M}(\eta^6\text{-}\mathrm{C_{10}H_8})_2]$; M = V, Cr, Mo), and discovered their remarkable ability to function as "naked" metal atom reagents in reactions with carbon monoxide and other good acceptor ligands.[3] Subsequently, anionic versions were reported, including $[\mathrm{Zr}(\eta^4\text{-}\mathrm{C_{10}H_8})_3]^{2-}$,[4] $[\mathrm{Ta}(\eta^4\text{-}\mathrm{C_{10}H_8})_3]^-$ (**1**),[5] and $[\mathrm{Co}(\eta^4\text{-}\mathrm{C_{10}H_8})_2]^-$.[6] These latter species are of substantial interest in chemical synthesis as storable sources of atomic metal anions.[7] Thus, they are promising precursors to new classes of homoleptic metalates[8] or other compounds that may not be available by other routes, including metal-atom vapor syntheses.[9]

Efforts to extend this series of naphthalenemetalates to other transition metals have been hindered, often greatly, by their highly reactive and/or thermally unstable natures, particularly in solution. For example, homoleptic naphthalenemetalates of niobium and tantalum were originally proposed to be intermediates in the atmospheric pressure syntheses of the hexacarbonylmetalates(1−) from the respective $\mathrm{MCl_5}$ mediated by alkali-metal–naphthalene species.[10] Although the tantalum–naphthalene precursor was much later identified as **1**,[5] attempts to isolate and characterize a presumed homoleptic naphthaleneniobate(1−) (**2**) have so far failed.[11] However, a recent synthesis of the first well-defined naphthalenecobaltate(1−) ($[\mathrm{Co}(\eta^4\text{-}\mathrm{C_{10}H_8})(\eta^4\text{-cod})]^-$; cod = 1,5-cyclooctadiene), obtained by mixing cod with a thermally unstable precursor,[6] suggested that a similar approach might yield an unprecedented isolable napthaleneniobate, which could function as a convenient source of atomic $\mathrm{Nb^-}$ ions in chemical reactions.

The addition of variable amounts of cod to **2** under a variety of conditions did not lead to any tractable products, but treatment of orange-brown slurries of **2** in tetrahydrofuran at −78 °C with an excess (ca. 10 equiv) of trimethylphosphane ($\mathrm{PMe_3}$) afforded deep red-orange solutions, which persisted at room temperature for several hours. From this reaction mixture, the satisfactorily pure anion $[\mathrm{Nb}(\eta^4\text{-}\mathrm{C_{10}H_8})_2(\mathrm{PMe_3})_2]^-$ (**3**) was isolated in 60–70 % yields, based on $[\mathrm{NbCl_4(thf)_2}]$ [Eq. (1)] (DME = 1,2-dimethoxyethane) as a highly air-sensitive bright orange microcrystalline [Na(thf)] salt (see the Experimental Section). Compound **3** is significant as it is the only naphthalene derivative of the unknown homoleptic naphthaleneniobates $[\mathrm{Nb}(\eta^4\text{-}\mathrm{C_{10}H_8})_3]^-$ and $[\mathrm{Nb}(\eta^6\text{-}\mathrm{C_{10}H_8})_2]^-$, and is a precursor to an unprecedented niobium–butadiene complex (see below). It is also the first niobium–naphthalene complex to be described, which is surprising because numerous other niobium arenes have been reported[12] and several vanadium–[3,13] and tantalum–naphthalene[5,14] complexes are well-established. However, none of these prior complexes are analogous to **3**.

$$[\mathrm{NbCl_4(thf)_2}] + 5\,\mathrm{NaC_{10}H_8} \xrightarrow[\substack{-60\text{ to }+20\,^\circ\mathrm{C}\\ -4\,\mathrm{NaCl}\\ -\mathrm{DME}}]{\mathrm{DME}} [\mathbf{2}] \xrightarrow[\substack{\text{excess PMe}_3\\ -78\text{ to }+20\,^\circ\mathrm{C}}]{\mathrm{THF}} \underset{68\,\%\text{ yield}}{[\mathrm{Na(thf)}][\mathbf{3}]} \qquad (1)$$

The ^{1}H and ^{13}C NMR spectra of the 18-electron anion **3** are unexceptional and entirely consistent with its formulation, and show resonances characteristic of η^4-naphthalene[4,5] and $\mathrm{PMe_3}$ groups bound in a 1:1 ratio to an electron-rich metal center. Interestingly, the average ^{13}C chemical shifts and $J_{\mathrm{C\text{-}H}}$ values for the coordinated outer or 1,4-carbon atoms, which are particularly sensitive to the metal environment, suggest that the degree of metal to π*(diene) back-bonding, or $\sigma^2\pi$ character[15] of the coordinated naphthalene groups, is somewhat greater in **3** than in **1** or even the dianion $[\mathrm{Zr}(\eta^4\text{-}\mathrm{C_{10}H_8})_3]^{2-}$.[16] Thus, the presence of two good donor $\mathrm{PMe_3}$ groups appears to strengthen the metal–naphthalene interactions in **3**, compared to those in known homoleptic naphthalenemetalates and is likely to be an important factor in the stabilization of **3** relative to a homoleptic naphthaleneniobate(1−).

A single-crystal X-ray study on **3**, as the [Na([2.2.2]cryptand)]$^+$ salt, revealed normal cations, well-separated from two nearly superimposable independent anions, one of which is shown in Figure 1.[17] Structures of the anionic components confirmed the formulation of **3** derived on the basis of NMR spectroscopic and bulk elemental analytical data. Anion **3** has two equivalent η^4-naphthalene moieties bound to a niobium center, which has an approximate octahedral geometry with *cis*-$\mathrm{PMe_3}$ groups. Interatomic distances associated with the niobium–η^4-diene units in **3** show a normal long-short-long pattern in the C−C bonds, similar to that in **1**,[18] and characteristic of strong metal to diene back-bonding.[15] The corresponding Nb−C(diene) bonds have a definite long-short-short-long pattern, which is unusual among early-transition-metal–diene complexes,[15,19] but well-precedented in Wreford's crowded $\mathrm{Ta^I}$–naphthalene complex $[\mathrm{TaCl}(\eta^4\text{-}\mathrm{C_{10}H_8})(\mathrm{dmpe})_2]$ (dmpe = 1,2-bis(dimethylphosphano)ethane).[14,19] All other data for **3**, and the tantalum complex, indicate the presence of substantial metal–naphthalene back-bonding.[20,21]

Undoubtedly the most exciting reaction of **3** discovered to date, and one which establishes its utility as a storable source of naked $\mathrm{Nb^-}$ ions, is that with excess 1,3-butadiene, which affords the tris(butadiene)metal complex $[\mathrm{Nb}(\eta^4\text{-}\mathrm{C_4H_6})_3]^-$ (**4**). Anion **4** was isolated as satisfactorily pure microcrystalline colorless $[\mathrm{Na([18]crown\text{-}6)(thf)_{0.5}}]^+$ or orange $[\mathrm{N(PPh_3)_2}]^+$(PPN) salts (PPN = bis(triphenylphosphane)iminium) in 40–

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

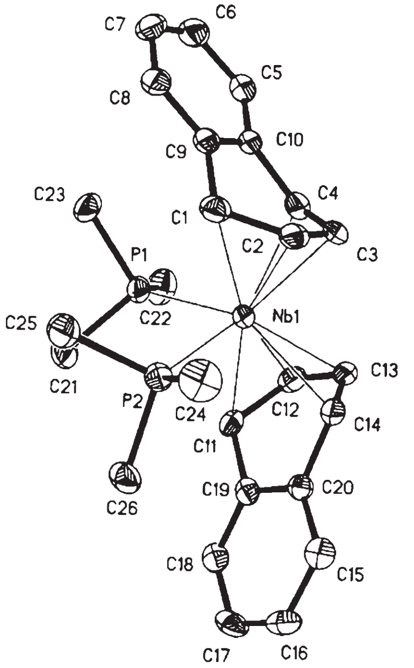

Figure 1. Molecular structure of anion **3**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Nb-C1 2.417(4), Nb-C2 2.285(3), Nb-C3 2.280(3), Nb-C4 2.400(3), Nb-C11 2.404(3), Nb-C12 2.290(4), Nb-C13 2.275(4), Nb-C14 2.390(4), Nb-P1 2.575(1), Nb-P2 2.573(1), C1-C2 1.456(5), C2-C3 1.395(5), C3-C4 1.456(5), C11-C12 1.455(5), C12-C13 1.402(5), C13-C14 1.442(5), P1-Nb-P2 93.38(3), Nb-centroid(η^4) 1.99, centroid(η^4)-Nb-centroid(η^4) 126.

50% yields [Eq. (2)].[22] The corresponding salts of the analogous tantalate $[Ta(\eta^4\text{-}C_4H_6)_3]^-$ (**5**) were obtained in

$$[Na(thf)][\mathbf{3}]+\text{excess } C_4H_6 \xrightarrow{\text{THF, 20°C}} \xrightarrow{[18]\text{crown-6}} [Na([18]\text{crown-6})(thf)_{0.5}][\mathbf{4}] \qquad (2)$$
$$46\%\ \text{yield}$$

60–70% yields from the interaction of **1** with 1,3-butadiene (see the Supporting Information for details). Although air-sensitive, these salts of **4** and **5** are quite thermally robust. For example, [PPN][**4**] has a melting point (with decomposition) of 190–193 °C. Products **4** and **5** are of interest as the first well-defined anionic homoleptic butadiene complexes of the early transition metals[23] and are isoelectronic with the long-known neutral Group 6 species $[M(\eta^4\text{-}C_4H_6)_3]$, M = Mo (**6**), W (**7**).[24] Subsequent experimental and computational studies on **6**, **7**,[25] and other butadiene complexes, particularly those of the early transition metals,[26] have shown that 1,3-butadiene is an outstanding acceptor ligand. As such, it qualitatively resembles carbon monoxide, and like the latter,[27] should be capable of providing anionic homoleptic complexes for most d-block elements. For this reason, it is astonishing that only three well-defined anions of this type have been previously reported, all for later 3d-block metals: $[Co(\eta^4\text{-}C_4H_6)_2]^-$,[28,29] $[Co(\eta^4\text{-}1,4\text{-}t\mathrm{Bu}_2C_4H_4)_2]^-$,[9] and $[Fe(\eta^4\text{-}C_4H_6)_2]^-$.[30]

The ^{1}H and ^{13}C NMR spectra of **4** and **5** are nearly identical, independent of the cation, and qualitatively match the spectra previously reported for **6** and **7**.[24,29,31] However, the chemical shifts for the outer 1,4-carbon atoms and associated hydrogen atoms in **4** and **5** appear markedly upfield relative to their naphthalene precursors, **1** and **3**, respectively, as well as **6** and **7**. Also, the $J_{\text{C-H}}$ value for the 1,4-carbon atoms in **5** (140 Hz)[32] is smaller than the corresponding values found for **1**, **3**,[16] **6**, **7**, or free butadiene,[33] and is indicative of a greater degree of sp^3 hybrid character for these carbon atoms in tantalate **5**.

Single-crystal X-ray studies confirmed the formulations of **4** and **5** as the $[Na(\text{dibenzo}[18]\text{crown-6})(thf)_2]^+$ [34] and $[PPN]^+$ [35] salts, respectively. Both sets of salts contain essentially identical anionic units (Figure 2 for **5**, as the complexed Na$^+$ salt), well separated from unexceptional cations. Only details of the structures of anions in the slightly better resolved sodium salts will be described herein. Anions **4** and **5** display a trigonal prismatic arrangement of ligands about the metal center, similar to that previously described for **1**[5] and **6**.[24b,25b] The M−C and C−C bonds in **4** and **5** show well-defined short-long-long-short and long-short-long patterns, respectively, typical for complexes of early transition metals with η^4-1,3-dienes.[15,19] Interestingly, both structural and NMR data suggest that the diene ligands in **4** and **5** have more dianion character than those in uncharged **6**.[36] However, it is significant that **4** and **5** have appreciably longer average (outer) M−C1/C4 bonds, 2.33(1) and 2.30(1) Å, respectively, than the corresponding bond, 2.22(1) Å, reported for the trigonal prismatic d^{0}M(V) complexes $[M(CH_3)_6]^-$, M = Nb, Ta,[37] in which only M−C σ bonding is present.[38] These and other data presented herein indicate that both M−C σ and π bonding in **4** and **5** are important, and computational studies will be necessary to shed more light on the electronic structures of these presently unique diamagnetic anions.

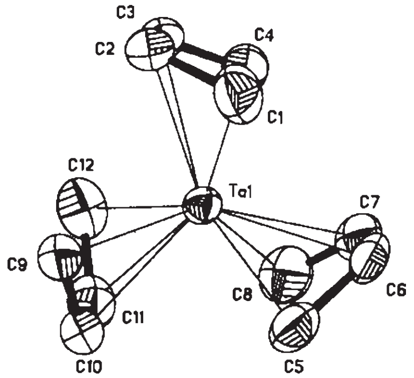

Figure 2. Molecular structure of anion **5**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ta-C1 2.288(5), Ta-C2 2.396(5), Ta-C3 2.412(5), Ta-C4 2.296(5), Ta-C5 2.281(5), Ta-C6 2.415(5), Ta-C7 2.415(5), Ta-C8 2.306(5), Ta-C9 2.301(5), Ta-C10 2.397(5), Ta-C11 2.400(5), Ta-C12 2.310(5), C1-C2 1.454(7), C2-C3 1.368(8), C3-C4 1.429(7), C4-C6 1.454(7), C6-C7 1.367(8), C7-C8 1.447(9), C9-C10 1.429(7), C10-C11 1.350(8), C11-C12 1.443(8), av Ta-centroid(η^4) 1.986, av centroid (η^4)-Ta-centroid(η^4) 120.

Details on the chemical properties of **4** and **5** will be described elsewhere, but it is noteworthy that they undergo facile protonation by triethylammonium chloride in THF to afford the previously known mixed 1-methylallyl-butadiene complexes $[M(\eta\text{-}1\text{-}MeC_3H_4)(\eta\text{-}C_4H_6)_2]$ M = Nb (**8**) and Ta (**9**) in good yields [Eq. (3)]. These neutral complexes may form

$$[M(\eta\text{-}C_4H_6)_3]^- + [Et_3NH]Cl \xrightarrow[-Cl^-,\ -Et_3N]{THF,\ 20\,^{\circ}C} [M(1\text{-}MeC_3H_4)(C_4H_6)_2] \quad (3)$$

8, 82 % yield

9, 59 % yield

via the intermediacy of the unknown isomeric hydrides $[HM(C_4H_6)_3]$, and are of particular significance to this research because they were originally prepared and isolated from the reactions of Nb and Ta atoms with excess 1,3-butadiene in a metal-atom reactor.[39] That these latter syntheses provided **8** and **9** rather than the evidently more reactive (and still unknown) neutral 17-electron homoleptic butadiene complexes, $[M(C_4H_6)_3]$ (M = Nb, Ta), provides a particularly striking example of where the use of anionic "naked" metal atom sources is of vital importance in permitting access to a previously unknown class of transition-metal compounds, namely, anions **4** and **5**.

In summary, we have prepared, isolated, and fully characterized the first naphthalene–niobium complex $[Nb(\eta^4\text{-}C_{10}H_8)_2(PMe_3)_2]^-$ (**3**), which was shown to be a useful storable source of atomic Nb^- ions in its reaction with 1,3-butadiene to afford the unprecedented homoleptic butadiene complex $[Nb(\eta^4\text{-}C_4H_6)_3]^-$ (**4**). The tantalum analogue $[Ta(\eta^4\text{-}C_4H_6)_3]^-$ (**5**) was also obtained from an analogous reaction of 1,3-butadiene with the labile naphthalenetantalate(1−) **1**. Compounds **4** and **5** are of additional interest because they are the first isolable homoleptic butadienemetalates of 4d and 5d metals. Their syntheses and the prior existence of late 3d metal homologues,[28–30] strongly suggests that homoleptic butadienemetalates should be available for many other d-block elements.

Experimental Section

2: This presently uncharacterized sodium naphthaleneniobate was obtained by the reaction of $[NbCl_4(thf)_2]$ with five equivalents of $NaC_{10}H_8$ in DME, as summarized in Equation (1). Details are provided in the Supporting Information.

3: A solution of PMe_3 (2.92 g, 38 mmol) in THF (100 mL, −75 °C) was added to solid **2** (5.19 g), also at −75 °C. The reaction mixture was slowly warmed to room temperature with stirring in an argon atmosphere over 13 h. Following filtration and evaporation of solvent (about 85 mL) under vacuum, pentane (100 mL) was added, with stirring, to precipitate the product as satisfactorily pure orange microcrystals of $[Na(thf)][Nb(\eta^4\text{-}C_{10}H_8)_2(PMe_3)_2]$ (2.64 g, 68 %, based on the amount of $[NbCl_4(thf)_4]$ employed to prepare **2**). Elemental analysis (%) calcd for $C_{30}H_{42}NaNbOP_2$: C 60.41, H 7.10; found: C 60.10, H 7.13. ^1H NMR (300 MHz, $[D_8]$THF, 20 °C, cation resonances omitted; Np = naphthalene) $\delta = 0.63$ (d, 18 H, PMe_3), 1.48 (m, 2 H, H1, H11, Np), 1.86 (m, 2 H, H4, H14, Np) 3.56 (m, 2 H, H2, H12, Np), 4.22 (m, 2 H, H3, H13, Np), 5.69, 5.76 ppm (m, 8 H, *exo*-benzene rings, Np); $^{13}C\{^1H\}$ (75 MHz, $[D_8]$THF, 20 °C). $\delta = 22.6$ (d, CH_3, PMe_3), 53.1 (C1, C11, Np), 61.4 (C4, C14, Np), 68.3 (C3, C13, Np), 81.0 (C2, C12, Np), 117.3, 118.0, 118.6 (*exo*-benzene rings), 152.5, 154.8 ppm (C9, C10, C19, C20, Np). $^{31}P\{^1H\}$ (121 MHz₃, $[D_8]$THF, 20 °C) $\delta = 5.1$ ppm (br s). The identification of C and H resonances was established by $^1H\text{-}^{13}C$ HMQC and COSY 2D NMR spectroscopy, as well as from trends previously established for η^4-naphthalene complexes,[4,5] but no unique assignments of the resonances for the *exo*-benzene hydrogen or carbon atoms were possible. X-ray quality single-crystals of **3** were obtained by treating [Na(thf)][**3**] (76 mg) with [2.2.2]cryptand (59 mg). The mixture was dissolved in THF (15 mL) and layered with pentane. Slow diffusion at 20 °C afforded suitable single crystals of [Na([2.2.2]cryptand)][**3**] within 5 days. These crystals possessed identical spectroscopic properties for the anionic component as the [Na(thf)] salt.

4: A solution of [18]crown-6 (0.263 g, 0.995 mmol) in THF (15 mL) was added to a solution of [Na(thf)][**3**] (0.527 g, 0.883 mmol) in THF (15 mL) in an atmosphere of argon. The argon was evacuated and 1,3-butadiene (500 mL) at 20 °C and 1 atm pressure (ca. 20 mmol) was introduced. After stirring the mixture for 23 h, excess pentane (100 mL) was added, which caused precipitation of an off-white solid. This was isolated by filtration, washed with pentane (2 × 5 mL), and dried under vacuum. An additional crystallization from THF/pentane afforded satisfactorily pure colorless solid $[Na([18]crown\text{-}6)(thf)_{0.5}]$[**4**] (0.253 g, 46 %). Elemental analysis (%) calcd for $C_{26}H_{46}O_{6.5}NaNb$: C 53.98, H 8.01; found: C 53.64, H 7.89. ^1H NMR (300 MHz, $[D_8]$THF, 20 °C, cation resonances omitted, integration of resonances consistent with bulk elemental analysis values) $\delta = -0.30$ (br m, 6 H, *endo*-H1, H4), 1.09 (M, 6 H, *exo*-H1, H4), 4.39 ppm (m 6 H, H2, H3) $^{13}C\{^1H\}$ (75 MHz, $[D_8]$THF, 20 °C, cation resonances omitted) $\delta = 35.7$ (br s, C1, C4), 105.2 ppm (s, C2, C3). X-ray quality single-crystals of **4**, as the $[Na(dibenzo[18]crown\text{-}6)(thf)_2]^+$ salt, were grown within 2 days as colorless plates from a pentane-layered THF solution at 20 °C. The latter salt was prepared by the same procedure shown above, except dibenzo[18]crown-6 was used instead of [18]crown-6 in the complexation step. The NMR spectra of **4** in these two salts were identical.

See the Supporting Information section for the preparation of **2**, from which well-defined salts of **3** were obtained; synthesis of $[PPN]^+$ salts of **4** and **5**; a figure of anion **4** in the $[Na(dibenzo[18]crown\text{-}6)(thf)_2]^+$ salt; synthesis of $[Na(crown\ ether)]^+$ salts of **5**; and protonation of **4** and **5** to produce **8** and **9**, respectively.

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[1] E. P. Kündig, P. L. Timms, *J. Chem. Soc. Chem. Commun.* **1977**, 912.

[2] C. Elschenbroich, R. Möckel, *Angew. Chem.* **1977**, *89*, 908; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 870.

[3] a) E. P. Kündig, P. L. Timms, *J. Chem. Soc. Dalton Trans.* **1980**, 991; b) N. P. D. Thi, S. Spichiger, P. Paglia, G. Bernardinelli, E. P. Kündig, P. L. Timms, *Helv. Chim. Acta* **1992**, *75*, 2593; c) M. Pomije, C. J. Kurth, J. E. Ellis, M. V. Barybin, *Organometallics* **1997**, *16*, 3582; d) M. V. Barybin, V. G. Young, Jr., J. E. Ellis, *J. Am. Chem. Soc.* **1998**, *120*, 429.

[4] M. Jang, J. E. Ellis, *Angew. Chem.* **1994**, *106*, 2036; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1973.

[5] W. W. Brennessel, J. E. Ellis, M. K. Pomije, V. J. Sussman, E. Urnezius, V. G. Young, Jr., *J. Am. Chem. Soc.* **2002**, *124*, 10258.

[6] W. W. Brennessel, V. G. Young, Jr., J. E. Ellis, *Angew. Chem.* **2006**, *118*, 7426; *Angew. Chem. Int. Ed.* **2006**, *45*, 7268, and references therein.

[7] Reactions of actual transition-metal atomic anions have been studied in the gas phase for many years and often provide remarkable transformations that have no precedent in condensed phases, see K. J. Fisher, *Prog. Inorg. Chem.* **2001**, *50*, 343.

[8] See, for example, the synthesis of the "all-inorganic" metallocene $[Ti(\eta^5\text{-}P_5)_2]^{2-}$: E. Urnezius, W. W. Brennessel, C. J. Cramer, J. E. Ellis, P. von R. Schleyer, *Science* **2002**, *295*, 832.

[9] Conventional reductions of neutral organometallic compounds, obtained from metal-atom vapor syntheses, to corresponding anions are well-established procedures, for example, for the conversion of bis(1,4-di-*tert*-butyl-1,3-butadiene)cobalt(0) into the corresponding anion, see F. G. N. Cloke, P. B. Hitchcock, A. McCamley, *J. Chem. Soc. Chem. Commun.* **1993**, 248. However, this indirect route to metalates is not possible when appropriate neutral precursors are very short-lived or otherwise inaccessible.

[10] C. G. Dewey, J. E. Ellis, K. L. Fjare, K. M. Pfahl, G. F. Warnock, *Organometallics* **1983**, *2*, 388.

[11] a) M. V. Barybin, J. E. Ellis, M. K. Pomije, M. L. Tinkham, G. F. Warnock, *Inorg. Chem.* **1998**, *37*, 6518; b) V. J. Sussman, PhD Thesis, University of Minnesota, **2007**.

[12] a) F. Calderazzo, G. Pampaloni, L. Rocchi, J. Strähle, K. Würst, *Angew. Chem.* **1991**, *103*, 109; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 102; b) F. Calderazzo, G. Pampaloni, L. Rocchi, J. Strähle, K. Würst, *J. Organomet. Chem.* **1991**, *413*, 91; c) F. Calderazzo, G. Pampaloni, *J. Organomet. Chem.* **1995**, *500*, 47; d) W. W. Brennessel, J. E. Ellis, S. N. Roush, B. R. Standberg, O. E. Woisetschläger, V. G. Young, Jr., *Chem. Commun.* **2002**, 2356.

[13] a) K. Jonas, V. Wiskamp, *Z. Naturforsch. B* **1983**, *38*, 1113; b) K. Jonas, W. Rüsseler, C. Krüger, E. Raabe, *Angew. Chem.* **1986**, *98*, 902; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 925; c) M. N. Bochkarev, I. L. Fedushkin, H. Schumann, J. Loebel, *J. Organomet. Chem.* **1991**, *410*, 321; d) M. N. Bochkarev, I. L. Fedushkin, V. K. Cherkasov, V. I. Nevodchikov, H. Schumann, F. J. Görlitz, *Inorg. Chim. Acta* **1992**, *201*, 69.

[14] J. O. Albright, S. Datta, B. Dezube, J. K. Kouba, D. S. Marynick, S. S. Wreford, B. M. Foxman, *J. Am. Chem. Soc.* **1979**, *101*, 611.

[15] M. Bochmann, *Organometallics 2. Complexes with Transition Metal-Carbon π-Bonds*, Oxford University Press, Oxford, **1994**, pp. 15–17.

[16] For example, the $J_{C1,C4\text{-}H}$ values for **1**[5], $[Zr(\eta^4\text{-}C_{10}H_8)_3]^{2-[4]}$, and **3** are 155, 151, and 146 and 141 Hz, respectively, where two values are shown for **3** because of the inequivalence of the outer diene carbon atoms (C1, C11, and C4, C14) in solution and in the solid state. The lower $J_{C\text{-}H}$ coupling constants for these carbon atoms in **3** indicate that they have more sp^3 hybrid character than the corresponding carbon atoms of **1** and the zirconate complex. Also, the average δC1/C4 value for **3**, 57.3 ppm, is shifted upfield relative to the corresponding values for **1**, 61.5, and the zirconate, 64.2 ppm, another measure of the very electron rich character of the niobium center.

[17] Crystal data for [Na([2.2.2]cryptand)][**3**]: $C_{44}H_{70}N_2NaNbO_6P_2$, $M_r = 900.86$, monoclinic, space group $P2_1$, red-orange wedge, $a = 15.772(2)$, $b = 17.932(2)$, $c = 17.533(2)$ Å, $\beta = 114.297(2)°$, $V = 4519.6(8)$ Å^3, $Z = 4$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 52728 reflections, 20246 independent, $R1 = 0.0356$ ($I > 2\sigma(I)$), $wR2 = 0.0796$ (for all data), $\mu = 0.394$ mm^{-1} (SADABS), full-matrix least-squares refinement on F^2. CCDC 657037 (**3**), 649039 (**4**), and 649040 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

[18] The average outer C1–C2 and inner C2–C3 bond lengths in **3** are 1.452(7) and 1.398(5), whereas the corresponding values in **1** are 1.452(8) and 1.365(5) Å,[5] respectively.

[19] Generally, complexes of this type have M–C(diene) bonds that show a short-long-long-short pattern.[15] However, the pattern may be weak, as in the case of **1**,[5] or even inverted, as in the case of **3** and $[TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2]$,[14] because the outer M–C(diene) bonds are elongated by bulky substituents on the dienes, for example, the *exo*-benzene group on η^4-naphthalene, and/or on the metal center, for example, organophosphane groups. For example, the average outer M–C1/C4 and inner M–C2/C3 bond lengths in **3** are 2.40(1) and 2.282(6), whereas the corresponding values for Wreford's tantalum naphthalene complex are 2.39(3) and 2.25(1) Å, respectively.

[20] For example, the fold angles of the naphthalene ligands for **3** and Wreford's tantalum complex are 39(1), and 43°, respectively, whereas the corresponding average fold angle for **1** is 44(1)°.[5] The magnitude of the fold angle, defined by the intersection of the planes of the η^4-diene and *exo*-benzene units in naphthalene complexes, is a qualitative indicator of metal–η^4-naphthalene back-bonding.[21] Much smaller fold angles are often observed in complexes of the later transition metals and η^4-naphthalene; for example, for $[Co(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-cod})]^-$, the value is 27°.[6]

[21] A. J. Deeming, *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, New York, **1982**, chap. 31.3, section 31.3.3.8. Although this discussion deals with structural and spectroscopic properties of iron–diene complexes, the conclusions are applicable to complexes of other transition-metal–dienes.

[22] Similar red-shifting in the color of carbonylmetalates has been reported to occur when alkali-metal ions are replaced by PPN$^+$ ions and are attributed to anion–PPN$^+$ charge transfer, see M. Tilset, A. A. Zlota, K. Foltung, K. G. Caulton, *J. Am. Chem. Soc.* **1993**, *115*, 4113. Note that the NMR spectra of **4** and **5** are independent of the cation (see later), thus, anion–PPN$^+$ interactions appear to have no significant effect on the molecular or electronic structures of these anions.

[23] Novel dilithio compounds $[Li(tmeda)]_2[M(C_4H_6)_3]$ (tmeda = $Me_2NCH_2CH_2NMe_2$) apparently only known in solution, were claimed on the basis of "IR and NMR spectroscopic studies to contain an η^2-bonded as well as two η^4-bonded C_4H_6 ligands," but no physical data or other information to support these formulations have been published in the scientific literature to date, see W. Gausing, G. Wilke, *Angew. Chem.* **1981**, *93*, 201; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 186.

[24] a) P. S. Skell, E. M. Van Dam, M. P. Silvon, *J. Am. Chem. Soc.* **1974**, *96*, 626; b) P. S. Skell, M. J. McGlinchey, *Angew. Chem.* **1975**, *87*, 215; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 195.

[25] a) J. C. Green, M. R. Kelly, P. D. Grebenik, C. E. Briant, N. A. McEvoy, D. M. P. Mingos, *J. Organomet. Chem.* **1982**, *228*, 239; b) M. Kaupp, T. Kopf, A. Murso, D. Stalke, C. Strohmann, J. R. Hanks, F. G. N. Cloke, P. B. Hitchcock, *Organometallics* **2002**, *21*, 5021.

[26] a) A. Nakamura, K. Mashima, *J. Organomet. Chem.* **1995**, *500*, 261; b) G. Erker, G. Kehr, R. Froelich, *Adv. Organomet. Chem.* **2004**, *51*, 109.

[27] a) W. Beck, *Angew. Chem.* **1991**, *103*, 173; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 168; b) J. E. Ellis, *Organometallics* **2003**, *22*, 3322, and references therein.

[28] K. Jonas, *Adv. Organomet. Chem.* **1981**, *19*, 97.

[29] P. W. Jolly, R. Mynott, *Adv. Organomet. Chem.* **1981**, *19*, 257.

[30] W. W. Brennessel, R. E. Jilek, J. E. Ellis, *Angew. Chem.* **2007**, *119*, 6244; *Angew. Chem. Int. Ed.* **2007**, *46*, 6132.

[31] B. Bogdanovic, H. Bönnemann, R. Goddard, A. Startsev, J. M. Wallis, *J. Organomet. Chem.* **1986**, *299*, 347.

[32] Unresolved $^{13}C\text{-}^{93}Nb$ coupling prevented acquisition of $J_{C\text{-}H}$ data for **4**.

[33] The $J_{C1,C4\text{-}H}$ values previously reported for **6**, **7**, and free butadiene are 155(2), 155(2),[29] and 156 Hz, respectively. For the last value, see J. B. Strothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, **1972**.

[34] a) Crystal data for [{[Na(dibenzo[18]crown-6)(thf)$_2$][**4**]}$_2$](thf): $C_{84}H_{124}Na_2Nb_2O_{17}$, $M_r = 1637.63$, monoclinic, space group $P2_1/c$, colorless plate, $a = 19.932(3)$, $b = 21.155(3)$, $c = 19.842(2)$ Å, $\beta = 97.165(2)°$, $V = 8301(2)$ Å^3, $Z = 4$, $T = 173(2$ K, λ=0.71073 Å, 94283 reflections, 18912 independent, $R1 = 0.0409$, $wR2 = 0.1176$ (for all data), $\mu = 0.351$ mm^{-1} (SADABS), full-matrix

least-square refinement on F^2; b) Crystal data for [{Na(dibenzo[18]crown-6)(thf)$_2$}[**5**]}$_2$](THF): $C_{84}H_{124}Na_2O_{17}Ta_2$, $M_r = 1813.71$, monoclinic, space group $P2_1/c$, colorless plate, $a = 19.945(3)$, $b = 21.171(3)$, $c = 19.829(3)$ Å, $\beta = 97.300(3)°$, $V = 8305(2)$ Å^3, $Z = 4$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 80075 reflections, 14683 independent, $R1 = 0.0385$, $wR2 = 0.0803$ (for all data), $\mu = 2.708$ mm^{-1} (SADABS), full-matrix least-squares refinement on F^2. See reference [17] for CCDC numbers and related information.

[35] Details on the X-ray studies of the [PPN]$^+$ salts of **4** and **5** will be described elsewhere: V. J. Sussman, J. E. Ellis, unpublished results. Crystal data for [PPN][**4**]: $C_{48}H_{48}NNbP_2$, $M_r = 793.72$, monoclinic, space group $P2_1/n$, orange needle, $a = 13.716(3)$, $b = 17.213(3)$, $c = 16.658(3)$ Å, $\beta = 90.217(3)°$, $V = 3933(1)$ Å^3, $Z = 4$, $T = 123(2$ K, $wR2$ (all data) = 0.0834 with GOF on F^2 of 1.050. Crystal data for [PPN][**5**]: $C_{48}H_{48}NP_2Ta$, $M_r = 881.76$, monoclinic, space group $P2_1/n$, orange plate, $a = 13.734(4)$, $b = 17.263(5)$, $c = 16.638(5)$ Å, $\beta = 90.218(3)°$, $V = 3945(2)$ Å^3, $Z = 4$, $T = 123(2)$ K, $wR2$ (all data) = 0.0675 with GOF on F^2 of 1.012.

[36] a) For example, in **5** the average outer and inner M–C bonds are 2.297(11) and 2.406(9) Å, respectively, whereas the corresponding values for **6** are 2.285(2) and 2.325(2) Å; b) for **5**, the average outer and inner C–C bond lengths are 1.44(1) and 1.36(1) Å, respectively, whereas analogous values for **6** are 1.414(4) and 1.403(5). The corresponding average M–C and C–C bond lengths for niobate **4** are close to those of **5**, but suggest that the niobium functions as a slightly weaker π donor than does tantalum in these complexes.

[37] S. Kleinhenz, V. Pfennig, K. Seppelt, *Chem. Eur. J.* **1998**, *4*, 1687.

[38] S. K. Kang, T. A. Albright, O. Eisenstein, *Inorg. Chem.* **1989**, *28*, 1613.

[39] a) P. R. Brown, F. G. N. Cloke, M. L. H. Green, *J. Chem. Soc. Chem. Commun.* **1980**, 1126; b) P. R. Brown, M. L. H. Green, P. M. Hare, J. A. Bandy, *Polyhedron* **1988**, *7*, 1819.